

Metal-insulator transitions in $\text{GdTiO}_3/\text{SrTiO}_3$ superlattices

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The density functional plus U method is used to obtain the electronic structure, lattice relaxation and metal-insulator phase diagram of superlattices consisting of m layers of Gadolinium Titanate (GdTiO_3) alternating with n layers of Strontium Titanate (SrTiO_3). Metallic phases occur when the number of SrTiO_3 layers is large or the interaction U is small. In metallic phases, the mobile electrons are found in the SrTiO_3 layers, with near-interface electrons occupying xy -derived bands, while away from the interface the majority of electrons reside in xz/yz bands. As the thickness of the SrTiO_3 layers decreases or the on-site interaction U increases a metal-insulator transition occurs. Two different insulating states are found. When the number of SrTiO_3 layers is larger than one, we find an insulating state with two sublattice charge and orbital ordering and associated Ti-O bond length disproportionations. When the number of SrTiO_3 units per layer is one, a different insulating phase occurs driven by orbital ordering within the quasi one-dimensional xz/yz bonding bands connecting Ti atoms across the SrO layer. In this phase there is no sublattice charge ordering or bond disproportionation. The critical U for the single-layer insulator is ~ 2.5 eV, much less than critical $U \sim 3.5$ eV required to drive the metal-insulator transition when the number of SrTiO_3 is larger than one. Inconsistencies between the calculation and the experiment suggest that many-body correlations may be important. A local inversion symmetry breaking around Ti atoms suggests the possibility of in-plane ferroelectric polarization in the insulating phase.

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I. INTRODUCTION

Complex oxide systems have been investigated extensively because of the variety of interesting phases that may be achieved by alloying and pressure¹. Of particular interest are materials with structures based on the ABO_3 perovskite motif (here A represents a rare earth or alkali atom, B a transition metal, and O an oxygen), because the many available possibilities for the A and B site ion lead to a great diversity of interesting properties. Over the last decade it has become clear that complex oxide heterostructures may be grown with precise layer-by-layer control of the composition²⁻⁵ enabling the creation of what are in effect new materials with potentially new properties. Moreover, carrier doping by charge transfer across interfaces can be much higher than that obtainable by alloying or vacancy formation in bulk materials^{4,6,7} while electronic gating allows the continuous control of carrier doping.⁸⁻¹² Heterostructures comprised of two different ABO_3 transition metal oxide perovskites with comparable bulk lattice constants have been reported to exhibit metal-insulator transitions (MIT)¹³⁻¹⁶, magnetism¹⁷⁻²⁰ as well as superconductivity.^{6,21}

The electronic properties of semiconductor heterostructures are determined by bulk band gaps, work functions, and the position of donor (acceptor) levels. In many transition metal oxides, electronic properties are, in addition, sensitive to structural features including octahedral rotation angles and transition-metal-oxygen bond lengths. Thus local structural changes across interfaces may play an important role in determining the electronic properties of oxide heterostructures. Moreover structural distortions propagate only a few lattice constants, so superlattice thickness has a structural as well

as a quantum confinement effect. Understanding the interplay of the various factors that contribute to metal-insulator transitions in oxide superlattices is an important open problem.

Heterostructures comprised of Mott-insulating GdTiO_3 (GTO) and band insulating SrTiO_3 (STO) provide an interesting model system. A single interface separating semi-infinite slabs of GdTiO_3 and SrTiO_3 is found to be metallic with sheet charge density about a half electron per in-plane unit cell,⁴ consistent with elementary ‘polar catastrophe’ notions of interface doping and in contrast with the more complicated behavior of the widely studied LaAlO_3 (LAO) systems, where the density of mobile carriers is much less than the polar catastrophe value¹³. Part of the issue may be that GdTiO_3 and SrTiO_3 share a common Ti–O network so that the main defects at an interface would be Gd–Sr antisite defects, which might be expected to disrupt the electron structure less than the Al–Ti antisite defects that might occur at the LAO-STO interface. A further interesting feature is that GdTiO_3 is itself a Mott insulator, and has a large amplitude rotational distortion away from the basic cubic ABO_3 perovskite structure. Taken together, these features suggest that the GTO–STO system may exhibit an interesting interplay of structural, interface, quantum confinement, and correlation effects, perhaps not too badly complicated by disorder, making it a suitable model system for investigation of general issues relating to metal-insulator transitions in oxide heterostructures.

Recently, thickness-dependent metal insulator transitions have been reported in GTO–STO heterostructures.⁵ As the thickness of SrTiO_3 decreases to two unit cells of SrTiO_3 , the interface is

found to become insulating. Both in metallic and in insulating interfaces, variations of the crystal structure that decay within several unit-cells of the interface are observed.²² In metallic interfaces, quantum oscillation measurements indicate that the conducting carriers move primarily in the plane of the interface.²³ The theory of the insulating phase was investigated on the basis of first-principles DFT+U calculations by Chen and Balents,²⁴ who proposed a novel dimerization mechanism that could lead to an insulating ground state when the number of SrTiO₃ layers, $n = 1$ and by Bjaalie *et al.*²⁵ who reported an insulating ground state with $n = 2$ using DFT with a hybrid functional. In this paper we present a more general DFT+U investigation of the metal-insulator phase diagram and structural properties of the GTO-STO system. Although DFT+U is a Hartree approximation which does not capture the full complexity of many-body physics, it enables the investigation of the interplay between structural relaxation and electron correlation effects. The changes in the electronic structure in different structural phases are investigated and the spatial distribution of the electron gas and its orbital polarization for different thickness of SrTiO₃ are determined as function of interaction strength, U .

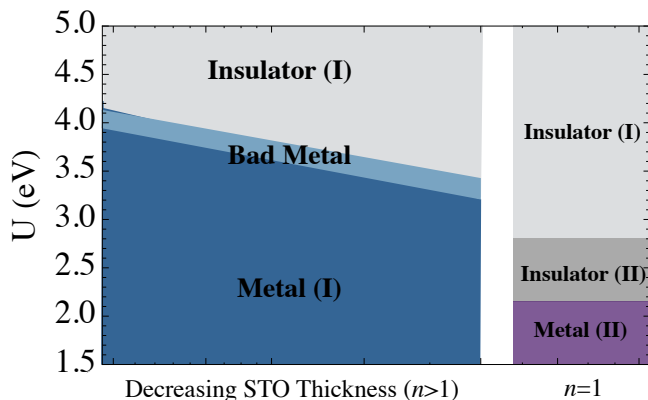


FIG. 1: (color online) Schematic phase diagram of electronic phases as a function of SrTiO₃ layer thickness n and on-site Coulomb repulsion U .

Our crucial finding, illustrated in Fig. 1, is that there are two different insulating phases, one occurring for ultra-thin ($n = 1$) and one for thicker ($n > 1$) STO layers. In the DFT+U approximation employed here, some form of charge, orbital, or magnetic ordering is required to stabilize insulating phases. When there is more than one SrTiO₃ unit cell ($n > 1$), we find a MIT from ferromagnetic metal to charge-ordered insulator with a narrow intermediate regime of charge ordered low density of states behavior, which we interpret as the signature in this calculations of a “bad metal” phase.^{26,27} The metal-insulator transition is accompanied by a structural transition resulting in sublattice bond disproportionation, and

within DFT+U the charge ordering is the main driving force for insulating/bad-metallic behavior. In the case of a single SrO layer ($n = 1$) we find two insulating phases. In one of them, yz/xz orbitals on opposite sides of the SrO layer form bonding and antibonding states; the antibonding states are empty and the spin-polarized half-filled bonding bands become gapped by orbital ordering. This transition from ferromagnetic metal to ferromagnetic insulator phase is consistent with the previous Hartree-Fock calculations of Chen and Balents.²⁴ The critical interaction strength required to drive this insulating phase is significantly lower than that needed to drive the insulating phase I. As on-site Coulomb interaction increases at $n = 1$ a transition occurs to a different insulating phase, characterized by two-sublattice charge order and similar to the insulating phase found at $n > 1$.

The rest of the paper is organized as follows. In section II we state the calculation methods that we use. Section III presents structural phase transitions in the different crystal structures. Electronic structures in each phase are presented in Section IV. Section V is devoted to an analysis of the electronic structure with a single SrO layer. In Section VI we present structural and electronic phase diagram in terms of layer thickness and electron correlation. Section VII presents possible ferroelectric polarization from broken inversion symmetry and centrosymmetry. In Section VIII we discuss a simplified view of metal insulator transition based on band alignment, followed by summary in Sec. IX.

II. CALCULATIONAL METHODS

The electronic structure and atomic structures are calculated using the GGA+U method as implemented in the Vienna *ab-initio* simulation package (VASP).^{28,29} We use a plane wave basis set with energy cutoff 500 eV and the projected augmented wave method. For all superlattices we use a unit cell $\sqrt{2} \times \sqrt{2} \times 2l$ (l : integer) structure to describe proper octahedral rotations and orbital ordering of the superlattices. All the structures are fully relaxed while the in-plane lattice constant is constrained to the substrate ($a = b = 3.86\text{\AA}$). Convergence is reached if the energy difference between two consecutive iterations is within 0.1 meV for electronic iterations and 1 meV for ionic relaxations. The minimum k -point grid size is $6 \times 6 \times 2$. For on-site Coulomb interaction the rotationally invariant form³⁰ is used for Ti- d orbitals. We treat the Hubbard U as an adjustable parameter while fixing the value of J as 0.6 eV.

III. LATTICE STRUCTURES

In this section we investigate the lattice structures of (GTO) _{m} (STO) _{n} superlattices for different n and different electronic phases. We begin with a brief discussion of the bulk structures. For SrTiO₃ we focus on the high

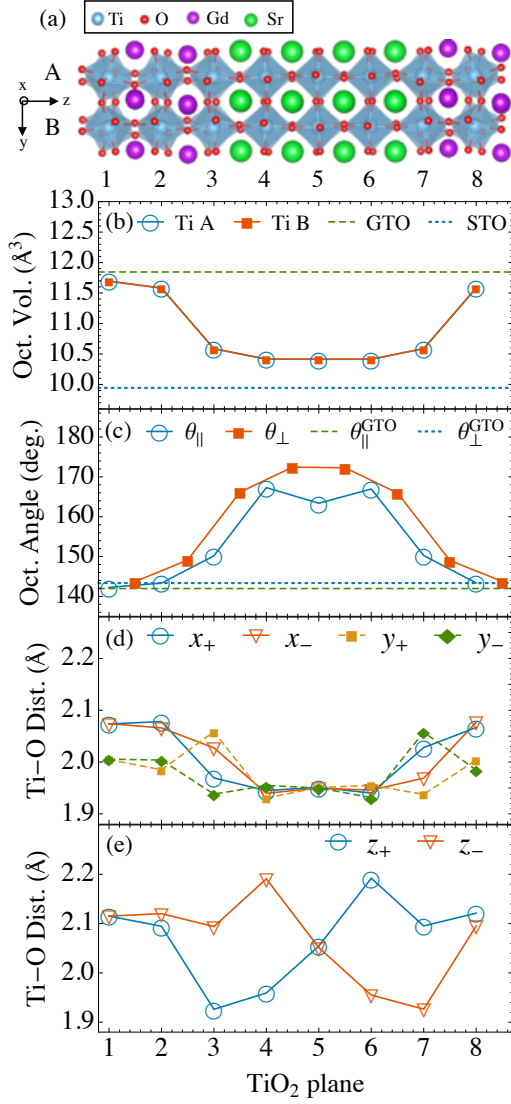


FIG. 2: (color online) Structural properties of (GTO)₄(STO)₄ superlattices in the metallic phase of the superlattice computed as described in the main text with $U = 3$ eV. (a) The atomic structure of the superlattice. A and B represent two inequivalent in-plane Ti atoms and the numbers in the bottom label the TiO₂ planes. (b) Octahedral volumes around A and B sublattice Ti atoms. The green dashed and blue dotted lines are respectively the octahedral volumes of bulk GTO and STO calculated with experimental in-plane lattice constant. (c) Average values of in-plane (θ_{\parallel}) and out-of-plane (θ_{\perp}) Ti-O-Ti angles. The green dashed and blue dotted lines are the in-plane and out-of-plane octahedral angle calculated for bulk GTO with experimental substrate, respectively. (d) In-plane (x, y) Ti-O bond lengths of A sublattice Ti atoms. (e) Out of plane (z) bond lengths of A sublattice Ti atoms. The six oxygen atoms around the each Ti atom are labeled by the direction from Ti to oxygen atoms expressed by $x_{\pm}, y_{\pm},$ and z_{\pm} where the direction (x, y, z) and subscripted sign represent pseudo-cubic axis defined in panel (a) and plus and minus direction, respectively. Exchanging x_{\pm} to y_{\mp} gives the B sublattice Ti-O distances.

temperature phase which is nearly cubic with a crystallographic unit cell containing one Ti ion and an octahedral volume of $\sim 9.9 \text{ \AA}^3$. (In bulk STO, a transition occurs at $T \sim 110\text{K}$ to a lower symmetry phase only slightly distorted from the high temperature structure.³¹ The differences between the high and low T phase are not important for our discussion.) GdTlO₃ is strongly distorted away from the cubic perovskite structure, with a unit cell containing two Ti ions, a Ti-O-Ti bond angle $\approx 145^\circ$ and a substantially increased octahedral volume $\sim 11.3 \text{ \AA}^3$. Further GdTlO₃ displays a high degree of $(\pi, \pi, 0)$ “orbital ordering”, involving a two sublattice pattern in which in a plane (which we take to be perpendicular to the growth direction) the Ti-O bonds in the x direction are elongated on one Ti sublattice and compressed on the other, with the bonds in the y direction behaving oppositely. The differences in the octahedral rotations will be seen to have important consequences. To capture these we choose a $\sqrt{2} \times \sqrt{2} \times 2l$ (l : integer) computational unit cell such that the two inequivalent Ti ions lie in the plane perpendicular to the growth direction.

Fig. 2 presents relaxed lattice structures obtained using a moderate $U = 3$ eV so that the superlattice is metallic. The top panel (a) gives atomic positions. The second panel (b) shows that the octahedral volume changes discontinuously across the interface, taking essentially the bulk GdTlO₃ value for Ti ions bounded on all sides by Gd ions and taking essentially the bulk SrTiO₃ value for Ti ions either bounded on all sides by Sr ions, or at the interfaces with two Gd and two Sr neighbors. The spatial variation of the structure is related to the band alignments, which are such that the charge density for all Ti ions with eight Gd neighbors takes essentially the bulk GdTlO₃ value. We will show below that the correlation effects expressed here by the U make an important contribution to the band alignments. The third panel (c) shows the variation of the Ti-O-Ti bond angle for both bonds in the planes (θ_{\parallel}) and along the growth direction (θ_{\perp}). We see again that the bond angle deviates significantly from the bulk GdTlO₃ value only in Ti layers surrounded by Sr or for “apical” oxygens connecting an interface Ti to a Sr.

The remaining panels show Ti-O bond lengths. Bulk GdTlO₃ has a two-sublattice orbital ordering; our computational unit cell is such that the ordering wavevector is perpendicular to the growth direction (as is physically reasonable), and the resulting order is an in-plane xz/yz alternation. Fig. 2 (d) shows the in-plane bond lengths for one of the two sublattices. We see that in the GdTlO₃ region (layers 1,2,8) the Ti-O bond length in the plus and minus x directions is $\sim 0.1 \text{ \AA}$ greater than the Ti-O bond length in the plus and minus y directions (on the other sublattice, the pattern is reversed). Similarly within the SrTiO₃ (layers 4,5,6) there is negligible bond-length disproportionation. Thus as far as the in-plane bonds are concerned, the lattice distortions associated with GdTlO₃ propagate only as far as the in-

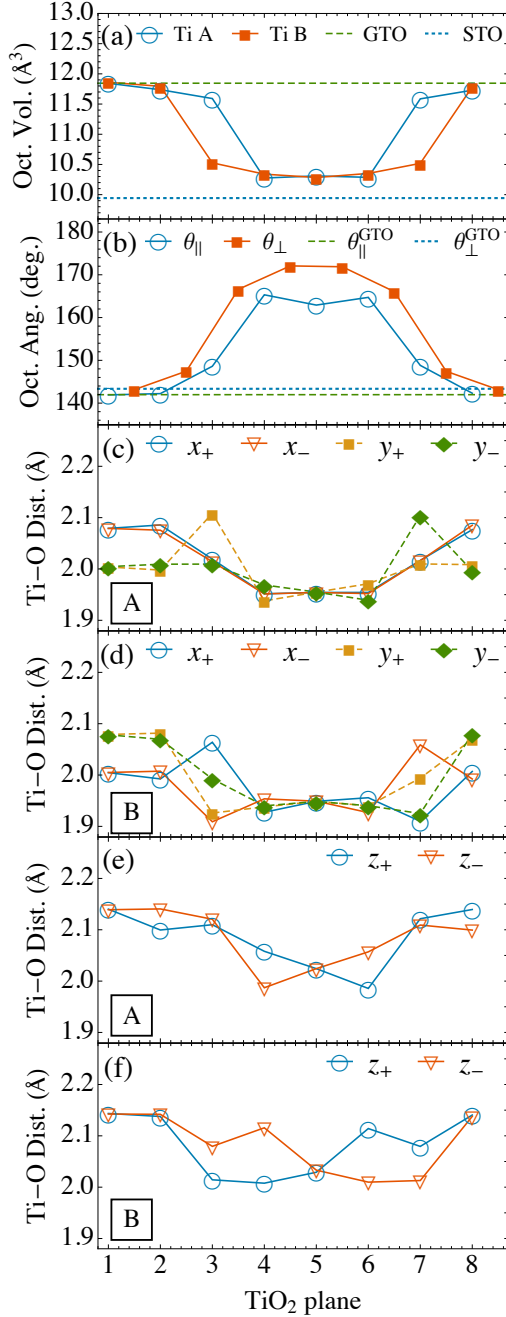


FIG. 3: (color online) Structural properties of $(\text{GTO})_4(\text{STO})_4$ superlattices in the insulating phase computed as described in the main text with $U = 4$ eV. Atomic coordinates are same as shown in Fig. 2. (a) Octahedral volumes around A and B sublattice Ti atoms. The green dashed and blue dotted lines are respectively the octahedral volume of bulk GTO and STO calculated with experimental in-plane lattice constant. (b) Average values of in-plane (θ_{\parallel}) and out-of-plane (θ_{\perp}) Ti-O-Ti angles. The green dashed and blue dotted lines are the in-plane and out-of-plane octahedral angle for GTO calculated with experimental substrate, respectively. (c-f) Ti-O distance between A and B sublattice Ti atoms following the same definition in the Fig. 2.

interface layer, consistent with what was observed for the bond angles and octahedral volumes.

However, the in-plane bonds in the interface layer and the out-of-plane bonds throughout the SrTiO_3 region show an interesting behavior implying breaking of the local inversion symmetry at the Ti site. The inversion symmetry breaking in the z direction may be understood in terms of the dielectric properties of SrTiO_3 . The electric fields associated with the polar discontinuity of the $\text{GdTiO}_3/\text{SrTiO}_3$ interface and the associated induced charges are partly screened by polar modes of the SrTiO_3 lattice (in particular an off-centering of the Ti) as discussed in Okamoto *et al.*³². Our new finding is a difference in the x and y bonds implying a spontaneous ferroelectric distortion in the plane. We also note that there is no difference in the octahedral volumes between A and B sublattices implying equal electron occupancy of the A and B sublattice Ti states. We define this structure with the same octahedral volume for A and B sublattices as the non charge-ordered (NCO) phase.

In Fig. 3 we present the structural properties of insulating $(\text{GTO})_4(\text{STO})_4$ superlattices obtained using DFT+ U with $U = 4$ eV. The variation of octahedral volume is very similar to that found in the previous metallic case, except that in the interface layer a clear difference between sublattices is visible. One sublattice (“A”) has almost the same octahedral volume as in bulk GdTiO_3 while the other has almost the same octahedral volume as bulk SrTiO_3 . This difference reflects the almost complete charge order noted by many previous studies of related interfaces including $\text{LaAlO}_3/\text{SrTiO}_3$ ³³ and $\text{LaTiO}_3/\text{SrTiO}_3$.³⁴ The difference in octahedral volumes has almost no effect on the in-plane bond angles; however the out of plane bond angles involving apical oxygens around interface Ti ions show small differences (about 3°) between A- and B- sublattices (not shown here.) The magnitude of the centrosymmetry breaking distortions in the z -direction Ti-O bond is much less, reflecting the almost complete confinement of polar charge to the interface layer, strongly reducing the need to screen internal electric fields. We define this structure with inequivalent octahedral volumes as the charge order (CO) phase.

For general $(\text{GTO})_m(\text{STO})_n$ superlattices, the structural transition from the NCO to the CO phase is driven by increasing the on-site Coulomb interaction U . However for $n = 1$ superlattices with a single STO unit cell, the distortion around the interface is different when U is small. Fig. 4 shows the structure for the metallic interface found in a $m = 5, n = 1$ superlattice with $U = 2$ eV. As in the $n > 1$ case there is no difference in the octahedral volume between A and B sublattice but there is a small difference in octahedral volume between layer 3 and 4 mainly due to the difference in the Ti-O distance in z direction. This is different from the NCO phase of $n > 1$ superlattices in which the octahedral volumes of two interfaces are different. We define the structure as CO II phase. We also note that the amount of Jahn-

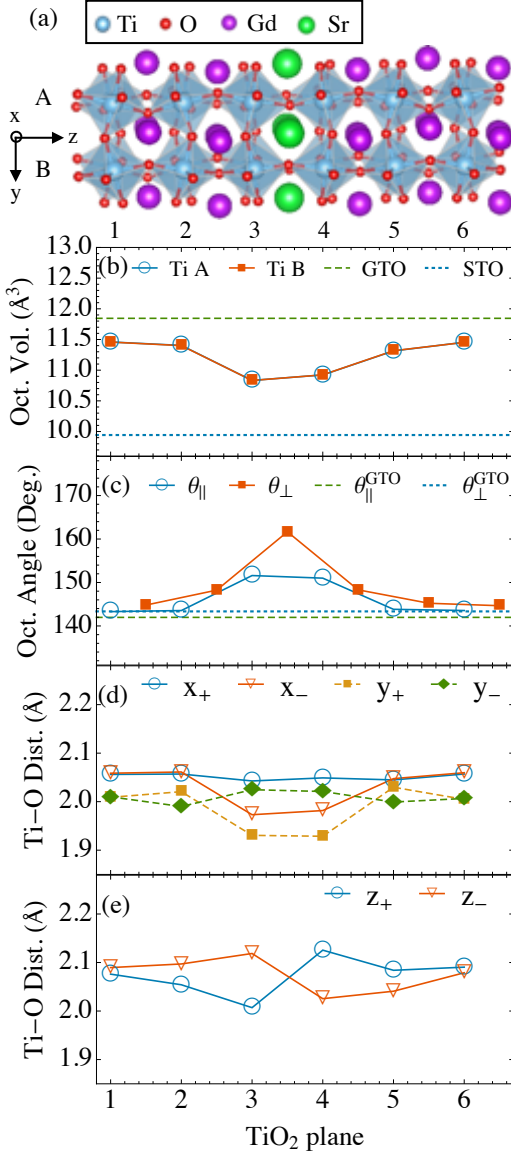


FIG. 4: (color online) Structural properties of $(\text{GTO})_5(\text{STO})_1$ superlattices computed as described in the main text with $U = 2$ eV. (a) The atomic structure of the superlattice. A and B represent two different in-plane Ti atoms and the numbers in the bottom denote TiO_2 plane number. (b) Octahedral volumes around A and B sublattice Ti atoms. The green dashed and blue dotted lines are respectively the octahedral volume of bulk GTO and STO calculated with the experimental lattice constant. (c) Average values of in-plane ($\theta_{||}$) and out-of-plane (θ_{\perp}) Ti-O-Ti angles. The green dashed and blue dotted lines are the in-plane and out-of-plane octahedral angle for GTO calculated with experimental substrate, respectively. (d-e) Distance between Ti and O in the in-plane (d) and growth direction (e) pseudo cubic direction of A sublattice Ti atoms. Exchanging x_{\pm} to y_{\mp} gives B sublattice Ti-O distances.

Teller distortion is much less in the GTO region due to the decreased correlation. As U increases, the structure changes to sublattice charge order (CO) phase as presented in Fig. 5. However unlike the $n > 1$ case the preferred orbital character is not switched between GTO and the larger interface octahedron since the Ti-O distance in x (y) direction are longer than y (x) for all octahedra in A (B) sublattice.

Figure 6 presents the critical electronic correlation U_c required to derive the structural phase transition between two distinct distortion patterns for $(\text{GTO})_m(\text{STO})_n$ superlattices. U_c is defined as the value of U in which the total energy with CO phase becomes lower than that with NCO (CO II) phase. The U_c is relatively insensitive to the thickness of GTO and we can see a general trend that U_c increases as the thickness of STO increases for $n > 1$. However, there is drastic decrease in the U_c for $n = 1$ superlattices. Thus we can identify two different groups of U_c ; one around 3.5 eV for $n > 1$ and around 2.5 eV for $n = 1$. The difference in the critical U and structural transitions for $n = 1$ and $n > 1$ superlattices implies that the change in the underlying electronic structures between two groups of superlattices will be different.

IV. ELECTRONIC STRUCTURE OF $n > 1$ GTO/STO SUPERLATTICES

This section presents the electronic structures of superlattices with two and more SrO layers. The CO distortion that we identified in the previous section plays an important role in localizing the electrons. The nominal valence counting implies that each GdO layer donates one-half electron per in-plane unit cell to each adjacent TiO_2 layer. Thus, the interface TiO_2 layer is doped by an half electron per in-plane Ti. Therefore within band theory both charge and orbital ordering are required to obtain insulating states. Further, as shown in panels (c) and (f) of Fig. 3, the apical oxygen is displaced in the z direction, implying the xy orbital is higher in energy than the xz/yz orbitals. Thus, in this case the electrons are in two orbitally degenerate bands and insulating behavior requires charge, spin, and orbital order.

Fig. 7 shows the total density of states (DOS) of a $(\text{GTO})_4(\text{STO})_4$ heterostructure with $U = 3$ (no charge order) and 4 eV (charge order). The Fermi energy is defined to be $E = 0$. The states in between -7.5 and -2.5 eV are oxygen p states and those near and above the Fermi energy are Ti- t_{2g} derived states. The oxygen p -states shifts about 0.5 eV as the values of U increases from 3 to 4 eV while the shift in energy of the Ti- t_{2g} states is about 0.2 eV. There are evident changes in DOS near Fermi energy. For $U = 4$ eV, the system is insulating with small gap less than 0.1 eV. For $U = 3$ eV, there are substantial increases in the density of states at the Fermi level and the system is a half-metal. As expected we find that the insulating ground state is associated with a volume difference in octahedra between interface A-B

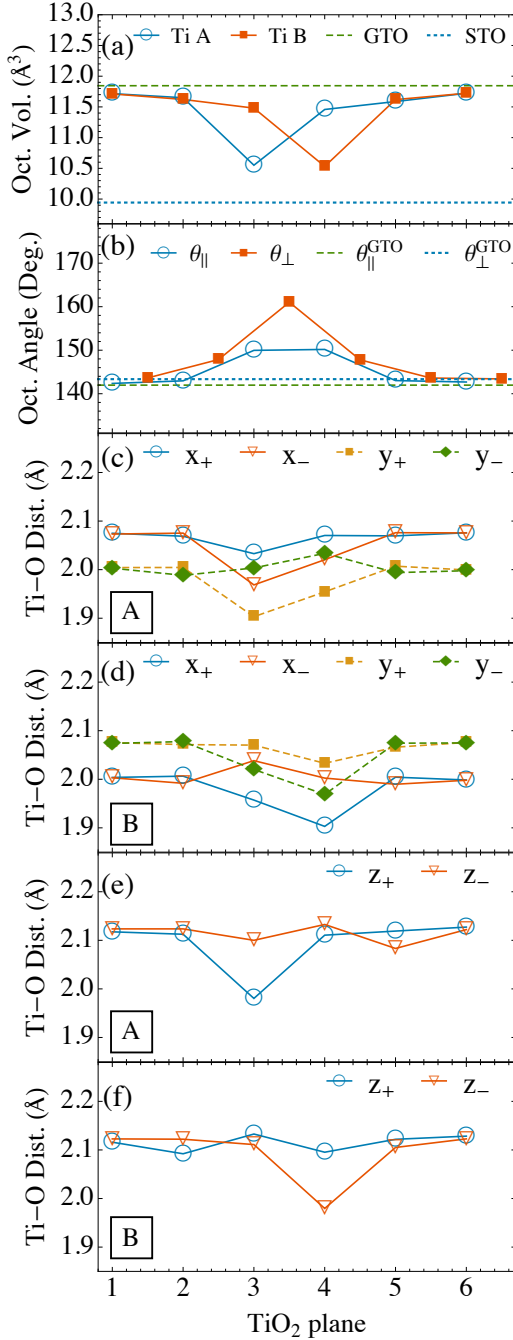


FIG. 5: (color online) Structural properties of $(\text{GTO})_5(\text{STO})_1$ superlattices in the insulating phase computed as described in the main text with $U = 3$ eV. Atomic coordinates are same as shown in Fig. 4. (a) Octahedral volumes around A and B sublattice Ti atoms. The green dashed and blue dotted lines are respectively the octahedral volume of GTO and STO calculated with the experimental lattice constant. (b) Average values of in-plane (θ_{\parallel}) and out-of-plane (θ_{\perp}) Ti-O-Ti angles. The green dashed and blue dotted lines are the in-plane and out-of-plane octahedral angle for GTO calculated with experimental substrate, respectively. (c-f) Distance between Ti and O in each pseudo cubic direction of A and B sublattice Ti atoms.

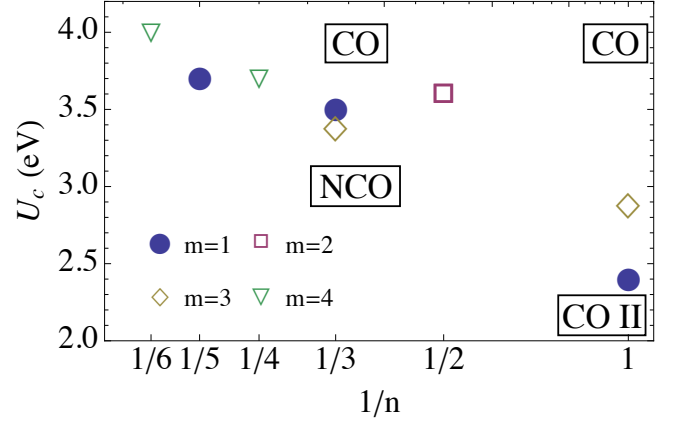


FIG. 6: (color online) Dependence of critical interaction strength U_c for the structural phase transition on the number n of STO layers in $(\text{GTO})_m(\text{STO})_n$ superlattices, computed as described in the text for different GTO thicknesses m (shown with different symbols indicated in Figure legend). For $U < U_c$ the phase is either not charge ordered (NCO), for $n > 1$ or weakly charge ordered (CO2) for $n = 1$. For $U > U_c$ the phase is strongly charge ordered (CO) at all n .

sublattice, while in the metallic ground state all octahedra have equal volumes.

In order to investigate the nature of the conducting interface, we present the projected density of states (PDOS) of $\text{Ti-}t_{2g}$ derived bands for $U = 3$ eV in Fig. 8. For the A-sublattice Ti atoms in between GdO layers (panel (b) and (c) labeled as A1 and A2), the density of states is similar to that of bulk GTO (panel (a)) with negligible density of state at the Fermi level and is orbitally ordered (xz on A-sublattice, yz on B-sublattice). The sublattice orbital ordering disappears for Ti atoms at the interface and in between SrO layers. At the interface (panel (d)), the xy -derived band is dominantly occupied and away from the interface the occupancy of yz/xz electrons is gradually increasing (panel (e-f)). These characteristic features of the PDOS are also found in other conducting superlattices with $n > 1$.

In Fig. 9, we present the layer resolved occupation of the t_{2g} orbitals of $(\text{GTO})_4(\text{STO})_4$ and $(\text{GTO})_4(\text{STO})_6$ superlattices showing that the orbital disproportionation persists to relatively thick superlattices. To define the occupation we integrate the PDOS of $\text{Ti-}t_{2g}$ orbitals from -1 eV to Fermi energy and normalize the result so that the total integrated density of states equals two electrons. We find that for the relatively thick STO layers studied the total t_{2g} occupation does not vary much in the STO and interface region because the screening length is larger than the STO thickness. We believe that for both $(\text{GTO})_4(\text{STO})_4$ and $(\text{GTO})_4(\text{STO})_6$ superlattices this is an interface driven phenomenon similar to that found in $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces, which have a dominantly occupied xy orbital in the near-interface region and yz/xz orbitals away from the interface^{35,36}.

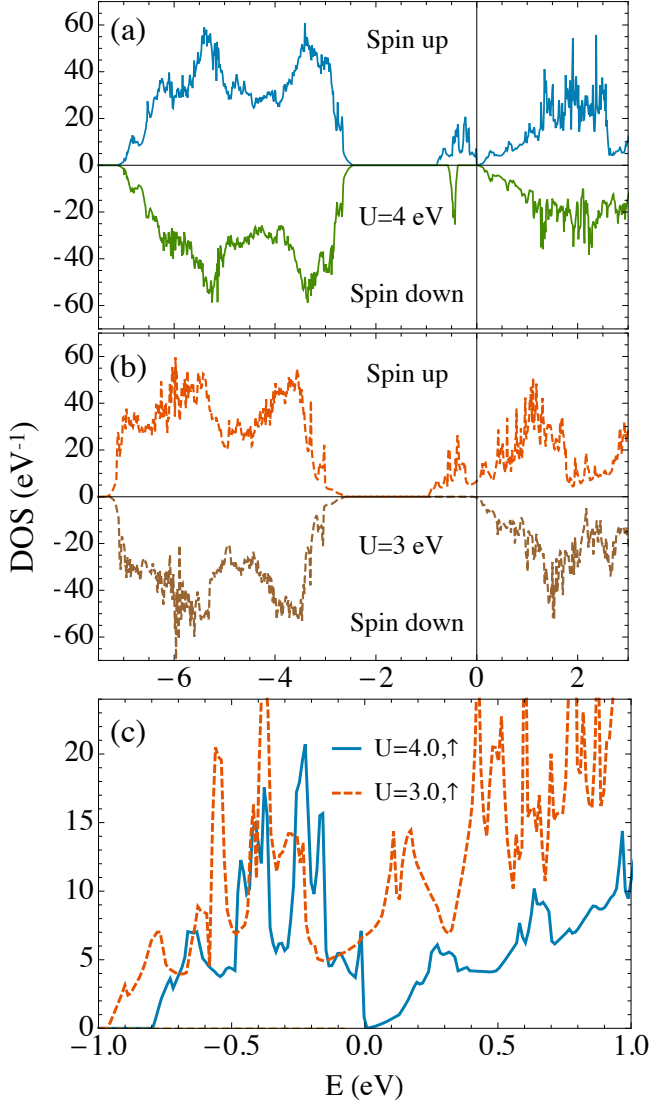


FIG. 7: (color online) Density of states of $(\text{GTO})_4(\text{STO})_4$ superlattices. (a) DOS for $U = 4.0$ eV. (b) DOS for $U = 3.0$ eV. (c) Comparison of spin up density of states near the Fermi energy.

Fig. 10 shows the PDOS of insulating ground state with $U = 4$ eV. In this phase we find that the electrons induced in the STO are tied to interface Ti atoms and exhibit sublattice orbital and charge ordering. As in the conducting interfaces, the PDOS of Ti sandwiched by GdO layers (panel (a) and (b)) resembles that of bulk GTO. At the interface, the Ti states of the larger octahedron (A3, panel (c)) are occupied with magnetic moment $0.82 \mu_B$ whereas the Ti states of smaller octahedron (B3, panel (d)) have negligible occupancy with magnetic moment $0.04 \mu_B$. Compared with the magnetic moment of Ti in the middle of GTO ($0.88 \mu_B$), we can consider the charge ordering as nominally one and zero electron for larger and smaller octahedron, respectively. The oc-

cupied Ti atoms have ferro-orbital (in this case yz) and ferromagnetic order but with spin direction opposite to that in the GTO region. As pointed out in the previous section, the change in the orbital character from xz to yz along the A sublattice (panel (b) and (c)) is related to the change in the bond disproportionation between GTO region and interface octahedra. This in turn enhances the localization of interface Ti states due to the small transfer integral between different t_{2g} orbitals. We note that the occupied states at the larger interface octahedron (panel (c)) have larger binding energy than the occupied states of GTO region (panel (a-b)) although the interface octahedral volume is slightly smaller than that of GTO region. Away from the interface the orbital and charge ordering disappears and the unoccupied t_{2g} bands are shifted closer to the Fermi energy. The PDOS for other $(\text{GTO})_m(\text{STO})_n$ interfaces with $n > 1$ are similar.

V. ELECTRONIC STRUCTURES WITH A SINGLE SrO LAYER

In this section, we present the electronic structure of $(\text{GTO})_5(\text{STO})_1$ superlattices. In these superlattices the critical U for structural transition is significantly lower than in superlattices with multiple SrO layers. Unlike the previous cases with $n > 1$, we will show that charge ordering is not a necessary condition for obtaining an insulating ground state and will show that the insulating phase persists to smaller U value due to the lack of low lying unoccupied states.

The major difference between the electronic structures for single and multiple SrO layers is the absence, in the single-layer case, of the states coming from Ti atoms in between SrO layers. This significantly decreases the critical of U for metal-insulator transition. Fig. 11 presents the DOS and PDOS of $(\text{GTO})_5(\text{STO})_1$ superlattices with $U = 3$ eV. From the total density of states we can see that the system is insulating with a band gap about 50 meV. As seen in the PDOS, the Ti atom surrounded by GdO layers (panel (b)) has a density of states similar to that of bulk GTO. In our results with $U = 3$ eV there exists both charge and orbital ordering but the difference in the magnetic moments of large ($0.75 \mu_B$) and small octahedra ($0.14 \mu_B$) is less than observed for $U = 4$ eV. This indicates that in-plane charge ordering is not crucial to the insulating phase. This conclusion is supported by the following argument. With two TiO_2 layers, yz (xz) orbitals in each layer form bonding and antibonding states with one dimensional dispersion in y (x) direction. Due to this one-dimensional spectrum, if the electrons are ferromagnetically ordered, the band is half-filled with strong Fermi surface nesting. Given that the inter-plane hopping is not significantly smaller than intra-plane hopping and xy band is higher in energy, a small orbital ordering that breaks the translation symmetry in both x and y direction and can open a gap at the Fermi energy. Thus as long as the octahedral distortion and electron correlation

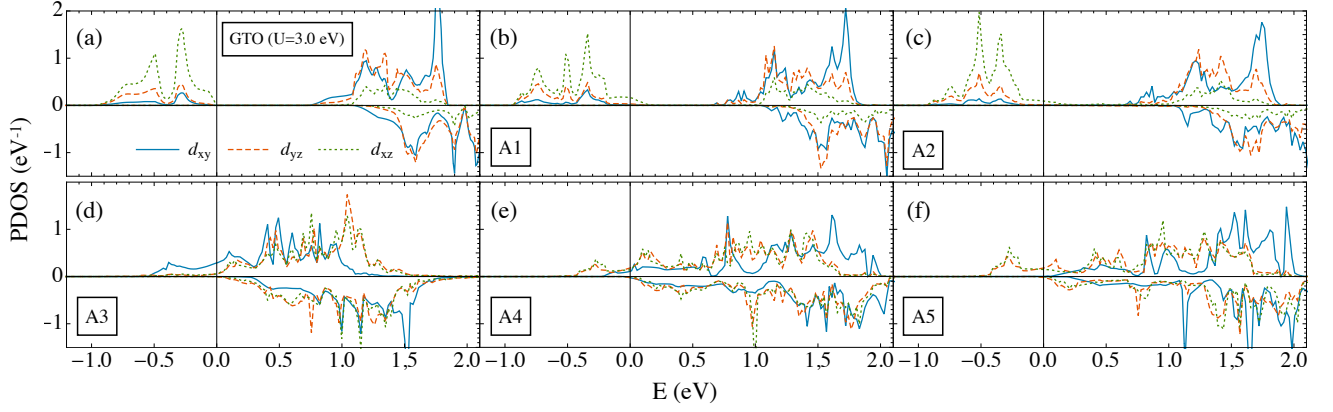


FIG. 8: (color online) Projected density of states (PDOS) of Ti- t_{2g} orbitals. The projection is done with t_{2g} orbital defined with pseudo cubic axes that deviate with octahedral coordinates but the change is not significant. Blue solid lines, red dashed lines, and green dotted lines represent d_{xy} , d_{yz} , and d_{xz} orbitals, respectively. (a) PDOS of GTO with $U = 3$ eV. (b-f) PDOS of $(\text{GTO})_4(\text{STO})_4$ with $U = 3$ eV for A-sublattice Ti atoms - numbers indicate atoms defined in Fig. 2.

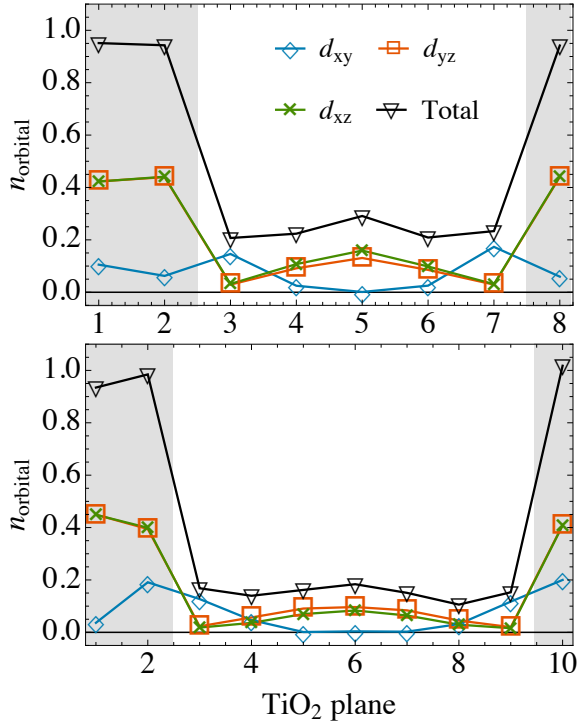


FIG. 9: (color online) Orbitaly resolved and total occupancy of Ti- t_{2g} states computed for $U = 3$ eV (metallic regime) of (a) $(\text{GTO})_4(\text{STO})_4$ and (b) $(\text{GTO})_4(\text{STO})_6$ superlattices. The gray region represents the Ti atoms between two GdO planes.

keep the xy band unoccupied, the system becomes insulating even at weak correlation. We note that adding an additional STO layer will make the system metallic with $U = 3$ eV since isolating a lowest t_{2g} band is much

harder because the low lying unoccupied band from the added STO layer will cross the Fermi energy. In other words, lack of low lying unoccupied states and separation of bonding and antibonding bands makes it possible for $n = 1$ superlattices insulating for lower U value. Our results are consistent with the previously reported Hartree-Fock calculation by Chen *et al.*²⁴ but for larger U we find sublattice charge ordering in addition to the orbital ordering.

VI. PHASE DIAGRAM FOR STRUCTURAL AND ELECTRONIC PHASES TRANSITIONS

In the section, we present a phase diagram summarizing our computed results for structural and electronic phases for $(\text{GTO})_m(\text{STO})_n$ superlattices. Fig. 12 shows the electronic and structural phase diagram in terms of critical U values and inverse of the STO layer thickness n . We can see that for $n > 1$, the MIT is accompanied by the structural transition which is crucial for the insulating phase. There is a narrow region of metallic phase before the structural transition with in-plane charge ordering for $n > 1$ superlattices but the density of state is small at the Fermi energy. We identify this as a bad metal.

Superlattices with a single SrO layer show qualitatively different phase behavior. Unlike the $n > 1$ case, there is no sharp change in the electronic structure across the structural transition from CO to CO II phase and the MIT occurs maintaining a weak layered charge order. This supports the idea²⁴ that charge ordering is not necessary for $n = 1$ superlattices. Moreover the value of the critical U for the MIT of the $n = 1$ superlattice is significantly smaller than $n > 1$ superlattices which also supports the idea that weak correlation can open the band gap at the Fermi energy. Experimentally there is a MIT

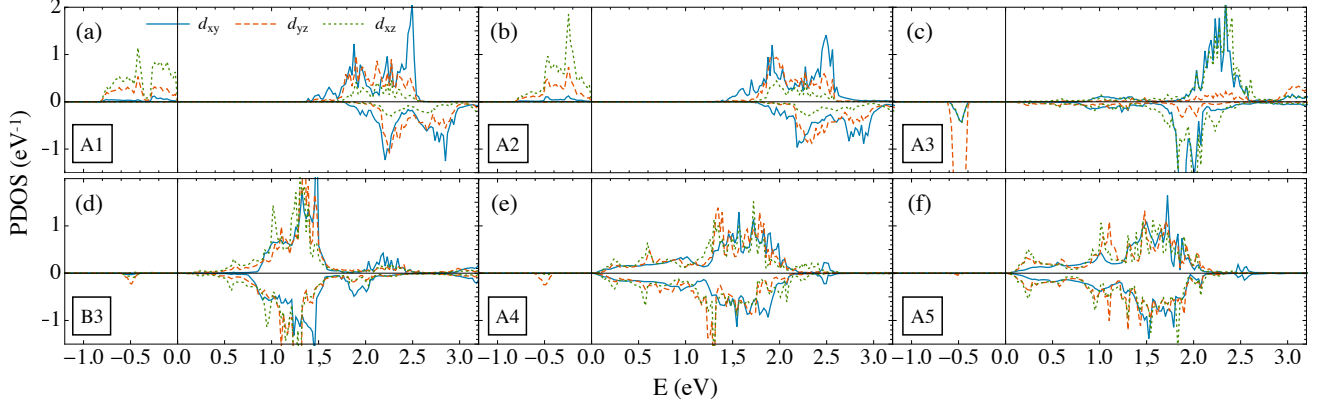


FIG. 10: (color online) (a-f) PDOS of Ti- t_{2g} orbitals for $(\text{GTO})_4(\text{STO})_4$ superlattice with $U=4$ eV following the atomic index defined in Fig. 2. The label at the bottom left of each panel represents Ti atoms where the letter A and B denote sublattice index and numbers indicate atoms defined in Fig. 2. Blue solid lines, red dashed lines, and green dotted lines represent d_{xy} , d_{yz} , and d_{xz} orbitals, respectively.

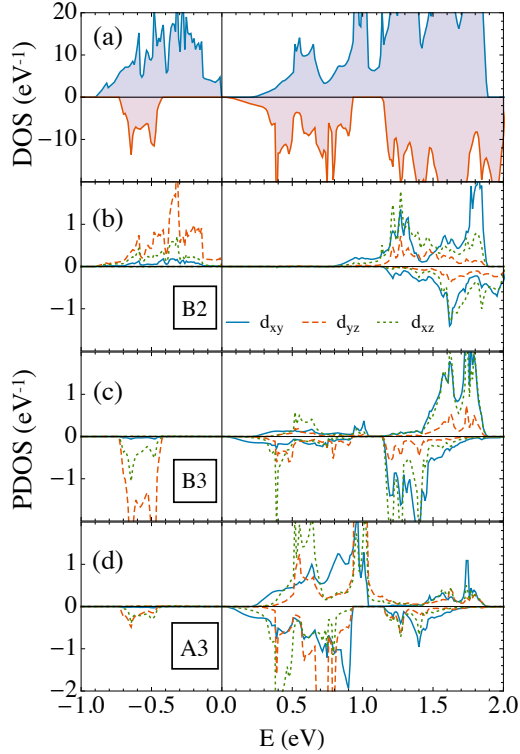


FIG. 11: (color online) Density of states of $(\text{GTO})_5(\text{STO})_1$ superlattices with $U = 3$ eV. (a) DOS near the Fermi level. (b-d) Projected density of states of Ti- t_{2g} orbitals for Ti positions defined in Fig. 4. Blue solid lines, red dashed lines, and green dotted lines represent d_{xy} , d_{yz} , and d_{xz} orbitals, respectively.

in between $n = 3$ and $n = 2$.³⁷ This is different from the prediction from the GGA+U phase diagram where the thickness dependent MIT occurs as the number of SrO layer changes from two to one.

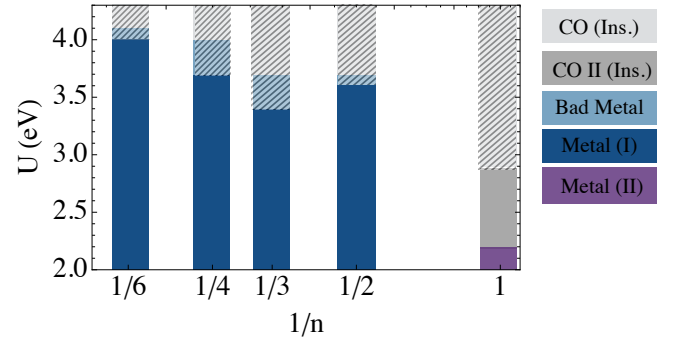


FIG. 12: (color online) Electronic and structural phase diagram for $(\text{GTO})_m(\text{STO})_n$ superlattices. We define in-plane and layered charge ordered insulating phase with orbital order as CO and CO II in gray and dark gray color, respectively. The structural CO phase is denoted as hatched lines so that the structural transition from CO phase to NCO (or CO II for $n = 1$) is expressed as the boundary of the shaded region. For $n > 1$, the narrow metallic region with charge ordering having very small density of state at the Fermi level is denoted as bad metal phase in light blue color. The ferromagnetic metal without charge ordering is denoted as metal phase in dark blue color and metallic phase with weak-layered charge ordering as metal II in purple. For the $n = 1, 3$ superlattices phase boundaries are obtained with $m = 2$, the $n = 2$ superlattice with $m = 2$, and $n = 4, 6$ superlattices with $m = 4$. The use of different m values is related to a small increase in the MIT phase boundary of $n = 2$ case.

VII. BROKEN INVERSION SYMMETRY AND FERROELECTRICITY

As can be seen from the Ti displacements in Fig. 2(d) or Fig. 3(c-d), in appropriate circumstances the superlattices we consider can develop non-centrosymmetric dis-

tortions leading to in-plane ferroelectric polarization. In bulk GTO, the Gd ions move substantially off center (~ 0.5 Å) relative to the ideal perovskite position due to the the $a^-a^-c^+$ octahedral rotation but the displacements alternate from layer to layer in the (001) direction so the effects cancel and there is no net polarization, and in particular the Ti atoms remain at center of the surrounding oxygen octahedron. Replacing a plane of Gd by Sr breaks the translation symmetry so that the polarization no longer cancels as previously suggested.³⁸ The symmetry breaking also leads to an off-centering of the Ti atoms, suggesting an additional ferroelectric component. This shift of Ti atoms suggests that there can be ferroelectric moment as in PbTiO_3 .

Fig. 13 shows atomic displacements of Ti and Gd atoms relative to the center of surrounding oxygen atoms for insulating $(\text{GTO})_4(\text{STO})_4$ ($U = 4$ eV) and $(\text{GTO})_5(\text{STO})_1$ ($U = 3$ eV) superlattices. In both superlattices, the shift is significant for near interface atoms. For out-of-plane direction, only interface Ti atoms are significantly displaced but the net moment is zero by the cancelation from the opposite contributions from two interfaces. For in-plane shifts, interface Ti atoms have the same displacement direction as that of Gd atoms next to the interface suggesting that the in-plane shift of Ti atoms is influenced by the movement of Gd atoms from the $a^-a^-c^+$ octahedral rotation. The magnitude of the in-plane shift is about 0.07 Å for Ti and 0.5 Å for Gd with $(\text{GTO})_4(\text{STO})_4$ superlattice and 0.03 Å for Ti and 0.5 Å for Gd atom with $(\text{GTO})_5(\text{STO})_1$ superlattice. For comparison, in PbTiO_3 the Ti and Pb atoms shift against the oxygen atoms about 0.26 Å and 0.42 Å, respectively.³⁹ Therefore we can see that the ionic shift is dominated by rare-earth atomic displacements. The amplitude of rare earth ion motion in our superlattices is comparable to that found in the canonical ferroelectric PbTiO_3 , but the amplitude of Ti atom motion in the superlattice is about a factor of 5 smaller than the corresponding motion in PbTiO_3 . There are also differences in ferroelectric polarization between the superlattices with even and odd number of STO layers. When there is an even number of STO layers, the net ferroelectric moment is zero due to the opposite polarization direction of two interfaces. Whereas with an odd number of STO layers, there is an in-phase shift from interface Ti atoms giving a small upward polarization and there is relatively larger upward polarization from the displacements of rare earth atoms. As seen in Fig. 13 (d) the uncompensated displacement of Gd atom located between the sixth and the first TiO_2 layer is larger than the displacement of Sr atom in between third and forth TiO_2 layers. Combined with the difference in nominal ionic charge between Gd (3+) and Sr (2+), there is a net upward polarization with an additional contribution from a small displacement of Ti atoms in layer 3 and 4 (Fig. 13 (c)). Therefore we expect that superlattices with an odd number of SrO layer, or more generally superlattices having two near interface Gd atoms displaced in the same direction may have a

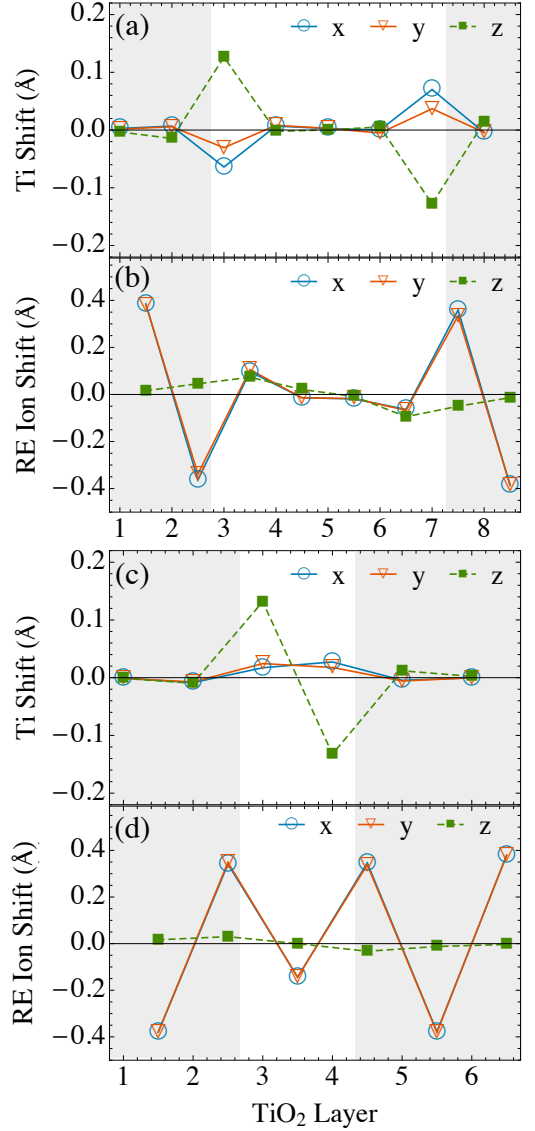


FIG. 13: (color online) The displacements of Ti and rare earth atoms (Gd, Sr) for insulating superlattices. (a-b) The displacements in $(\text{GTO})_4(\text{STO})_4$ superlattice with $U = 4$ eV. (c-d) The displacements in $(\text{GTO})_5(\text{STO})_1$ superlattice with $U = 3$ eV. The displacements of Ti and rare earth atoms are defined as the distance from the center of mass of nearest neighbor in-plane oxygen atoms. The shaded regions represent the bulk-like GTO region. The difference in the displacements between A and B sublattice is small so averaged values are shown.

net ferroelectric moment. In the calculations performed so far, the polarization lies in the xy plane, but ‘tricolor’ superlattices with Gd-Sr-X may also have a z -direction polarization.

VIII. BAND ALIGNMENT AND METAL-INSULATOR TRANSITION

In the polar catastrophe scenario of LAO/STO interfaces, a MIT occurs as the number of LAO layers increases.¹³ The MIT is caused by a change in the band alignment of the STO conduction band driven by an increase in the electrostatic potential proportional to the LAO thickness.^{35,40–42} Similarly we can think of the metal insulator transitions of $n > 1$ superlattices in terms of band alignments between the filled lower Hubbard band of GTO and the low-lying conduction band of STO. Fig. 14 shows the PDOS of oxygen p and Ti d orbitals in the bulk-like GTO region, at the interface, and bulk-like STO region. For the insulating interface, we can see that the lower Hubbard band of GTO in the bulk-like region lies slightly lower than the band bottom of conduction band in the bulk-like STO region. On the other hand, for metallic interfaces, the conduction band of the bulk-like STO region overlaps the occupied lower Hubbard band of the bulk-like GTO region. The band overlap is determined by four factors: the band gap in the GTO region Δ_g , Δ_{pd} defined as the energy difference between oxygen p bands and the middle of upper and lower Hubbard bands, Δ_{STO} denoting the band gap of STO, and E_{pol} defined as the energy shift in the top of oxygen p bands between GTO and STO region. We note that the energy shift E_{pol} arises from the dipole formed between GTO and STO. In the insulating phase, the energy shift is $\mathcal{E}d/2 \sim 2\pi e^2 n_{2D} d / \epsilon$ where \mathcal{E} is electric field between interface TiO_2 and adjacent GdO layer, d is Ti-Ti distance, ϵ is a dielectric constant, and n_{2D} is the sheet charge density of half electron per in-plane unit cell. In the metallic phase, electrons are delocalized over several layers of the STO region so the electric charge is farther from the interface and a larger dipole moment is expected. The energy shift is $\frac{4\pi e^2 n_{2D}}{\epsilon} \int_0^L dz \mathcal{E}(z)$ where L the distance from the GdO layer next to the interface to the TiO_2 plane at the center of STO. The estimated energy shift for insulating superlattice with four STO layers is about 155 meV by substituting the sheet charge density of 0.5 electron per in-plane unit cell and dielectric constant 75⁴³ and 388 meV for metallic superlattice by assuming uniformly distributed electron gas (as in Fig. 9). These values are consistent with the energy shift in Fig. 14 which is about 200 meV in the insulating superlattice and 700 meV for metallic superlattice. The factor of two differences may come from the uncertainty in the dielectric constant.

Thus, we can write the condition for obtaining an insulating superlattice as follows:

$$E_{pol} + \Delta_{STO}(n) > \Delta_{pd} - \Delta_g(U)/2.$$

Given that Δ_{pd} and E_{pol} is not sensitive to the value of U and n , we can see that the critical U for MIT increases as the thickness of STO increases since Δ_{STO} decreases as the number of STO layers n increases due to the confinement effect,⁴⁴ while Δ_g is proportional to U . Although we neglect the energy cost of octahedral

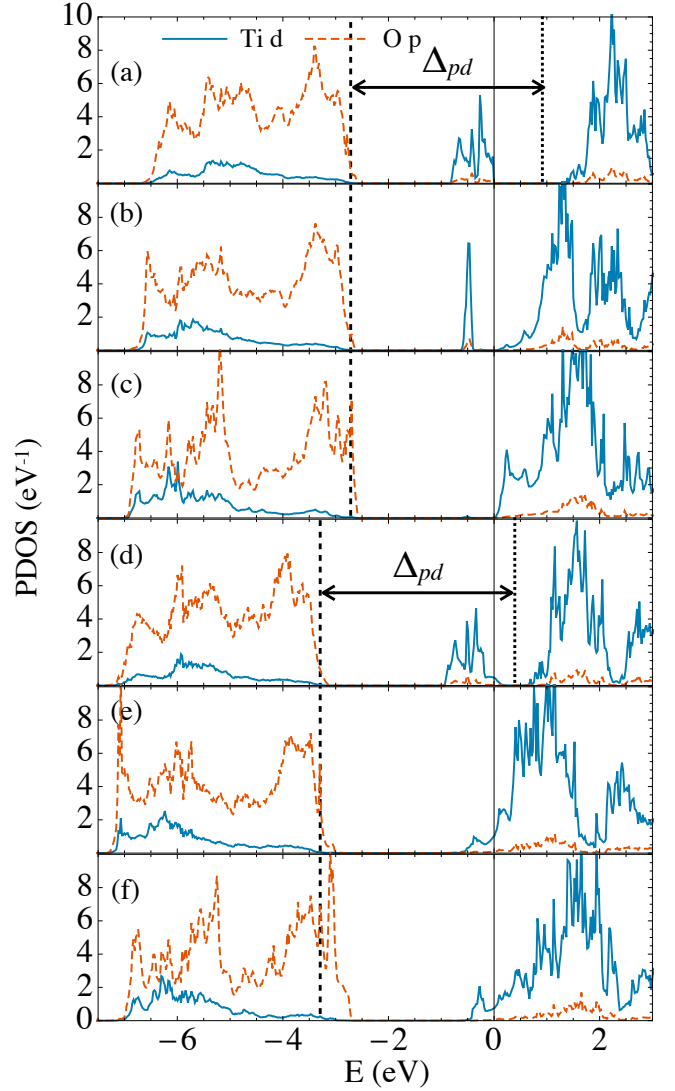


FIG. 14: (color online) PDOS of Ti d (blue solid line) and oxygen p (dotted red line) orbitals of $(\text{GTO})_4(\text{STO})_4$ superlattice. (a) PDOS in the middle of GTO with $U = 3$ eV and (b) $U = 4$ eV. (c) PDOS of interface TiO_2 layer for $U = 3$ eV and (d) $U = 4$ eV. (e) PDOS in the middle of STO for $U = 3$ eV and (f) $U = 4$ eV. The solid black line is the Fermi energy and the dashed black lines in the panel (a) and (b) represent the band edge of oxygen p orbital in the middle of GTO. The energy difference between the dashed black line and dotted black line (center of gap between lower and upper Hubbard bands) is defined as Δ_{pd} . In panel (e) and (f) the E_{pol} is defined as the energy difference of oxygen band edge of GTO and STO region.

distortion and energy gain from localizing electrons, this relation gives a reasonable estimate of the ground state of heterostructures between band and Mott insulator with bulk properties the materials.

IX. SUMMARY

We investigated the metal-insulator transition of GTO/STO superlattices using first-principles GGA+U method. Two different mechanisms for the insulating phase are identified. We find that charge and orbital ordering accompanied by difference in the volume of interface octahedra (“two sublattice charge order”) are necessary to obtain the insulating phase for superlattices with $n > 1$. On the other hand, in superlattices with $n = 1$ the insulating gap emerges via a combination of orbital ordering (leading to a quasi-one dimensional in-plane dispersion) combined with a bonding-and-tibonding splitting arising from coupling across the SrO layer, as previously found by Chen *et al.*²⁴. We find that the critical U needed to drive the MIT for $n = 1$ superlattices is significantly smaller than $n > 1$ since small orbital ordering can open a gap in the bonding band due to the instability in the one dimensional dispersion of yz/xz bands. A local inversion

symmetry breaking around Ti atoms is observed and it is shown that ferroelectric polarization is possible with odd number of STO layers. We present the phase diagram for general $(\text{GTO})_m/(\text{STO})_n$ and within GGA+U showing discrepancy between our results and the transport measurement of Ref. 37, which shows a metal insulator transition already at $n = 2$. The difference cannot be resolved by fine-tuning U implying the importance of additional physics not included in the DFT+U approximation.

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